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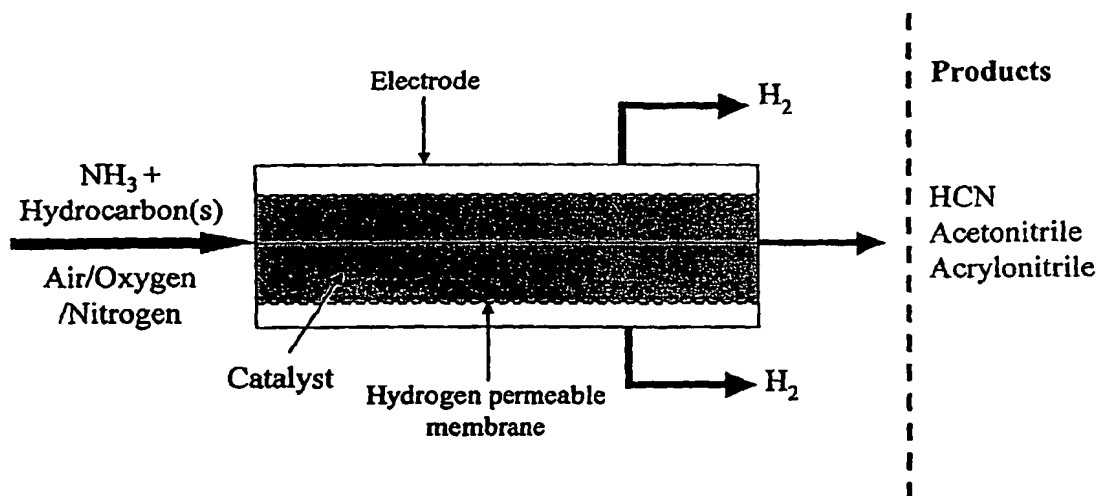
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(54) Title: SYSTEM AND METHOD FOR THE MANUFACTURE OF HYDROGEN CYANIDE AND ACRYLONITRILE WITH  
SIMULTANEOUS RECOVERY OF HYDROGEN



(57) Abstract: A system and method for the manufacture of hydrogen cyanide, acrylonitrile, and acetonitrile are provided. The system comprises at least one pulsed corona discharge reactor with each pulsed corona discharge reactor having a reaction zone. At least one reactant feed stream containing hydrogen is introduced into the pulsed corona discharge reactor and contacting the catalyst wherein hydrogen is removed from the reactant to form hydrogen cyanide, acrylonitrile, and acetonitrile.



— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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# SYSTEM AND METHOD FOR THE MANUFACTURE OF HYDROGEN CYANIDE AND ACRYLONITRILE WITH SIMULTANEOUS RECOVERY OF HYDROGEN

The present application is a continuation and claims priority of pending provisional patent application Serial No. 60/411,816, filed on September 18, 2003, entitled "System and Method for the Manufacture of Hydrogen Cyanide and Acrylonitrile with Simultaneous Recovery of Hydrogen".

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

This invention relates generally to system and method for the manufacture of hydrogen cyanide and acrylonitrile and, more particularly, the invention relates to system and method for the manufacture of hydrogen cyanide and acrylonitrile with simultaneous recovery of hydrogen in a pulsed corona discharge reactor.

### 2. Description of the Prior Art

Hydrogen cyanide is used for the production of chemical intermediates employed in the manufacture of nylon acrylic sheetings and coatings (methyl methacrylate), gold mining chemicals, animal feed supplements, water treatment, agricultural chemicals and herbicides, pharmaceuticals, household products, chelating products, among others. The annual production of cyanide (as HCN) actually exceeds 1.25 million metric tons per annum. Though several processes are available for the manufacture of HCN, the most popular are:

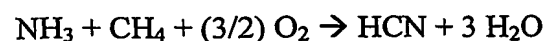
- **Shawnigan process:**

The following reaction is employed:

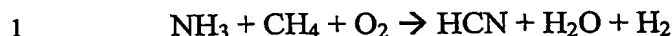


- **Andrussow process:**

This process, widely used for the manufacture of HCN, involves the use of the autothermal reactions of ammonia, methane and air over a platinum and rhodium gauze catalyst. The overall reaction can be represented as



A variant, with the addition of a lower amount of oxygen, leads to the formation of both hydrogen and water. Thus,



2           • **BMA process:**



4

5           HCN can also be produced as a by-product in the manufacture of acrylonitrile  
6 (ACN,  $\text{CH}_2=\text{CHCN}$ ) using the SOHIO process for the ammoxidation of propylene  
7 and ammonia. Air, ammonia and propylene are reacted in the presence of catalyst at 5  
8 – 30 psig, and temperatures of 1000 °F. Approximately, 1.5 billion pounds of ACN  
9 are produced each year in the U.S. alone. The major use is in the production of acrylic  
10 and modacrylic fibers – these fibers are marketed under the trade names Acrilan,  
11 Creslan, Verel, among others. Other uses include manufacture of acrylonitrile-  
12 butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resins, nitrile elastomers,  
13 and other chemicals. Acrylonitrile is also used as a fumigant.

14           In all these processes, as also noted earlier, platinum and rhodium based  
15 catalysts are necessary; in addition, high-temperature operation is required. The  
16 controlled addition of oxygen (air) provides the heat necessary for the reaction, and  
17 also permits regeneration of the catalyst.

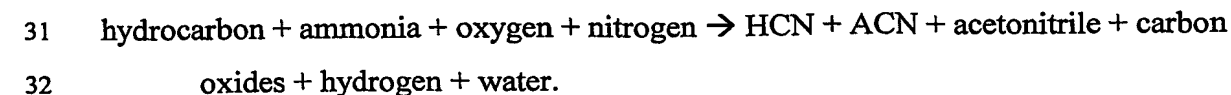
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19           SUMMARY

20           The present invention is a system for the manufacture of hydrogen cyanide,  
21 acrylonitrile, and acetonitrile. The system comprises at least one pulsed corona  
22 discharge reactor with each pulsed corona discharge reactor having a reaction zone.  
23 At least one reactant feed stream containing hydrogen is introduced into the pulsed  
24 corona discharge reactor and contacting the catalyst wherein hydrogen is removed  
25 from the reactant to form hydrogen cyanide, acrylonitrile, and acetonitrile.

26           In addition, the present invention includes a system for the manufacture of  
27 hydrogen cyanide, acrylonitrile, and acetonitrile. The system comprises a pulsed  
28 corona discharge reactor and a feed stream introduced into the pulsed corona  
29 discharge reactor wherein the following reaction is created:

30



33

1           The present invention further includes a method for manufacturing hydrogen  
2 cyanide, acrylonitrile, and acetonitrile. The method comprises providing at least one  
3 pulsed corona discharge reactor with each pulsed corona discharge reactor having a  
4 reaction zone, positioning a catalyst in the reaction zone, introducing at least one  
5 reactant feed stream containing hydrogen into the pulsed corona discharge reactor and  
6 contacting the catalyst, and removing hydrogen from the reactant to form hydrogen  
7 cyanide, acrylonitrile, and acetonitrile.

#### 8 9 BRIEF DESCRIPTION OF THE DRAWINGS

10           FIG. 1a is a schematic view illustrating a system and method, constructed in  
11 accordance with the present invention, wherein hydrocarbon and ammonia are the  
12 reactants;

13           FIG. 1b is a schematic view illustrating a system and method, constructed in  
14 accordance with the present invention, with the inclusion of a suitable solid phase  
15 catalyst within the reaction zone;

16           FIG. 1c is a schematic view illustrating a system and method, constructed in  
17 accordance with the present invention, with air, oxygen, and/or nitrogen being  
18 introduced;

19           FIG. 1d is a schematic view illustrating a system and method, constructed in  
20 accordance with the present invention, with a feed stream similar to FIG. 1c, but with  
21 use of a suitable solid phase catalyst in the reaction zone; and

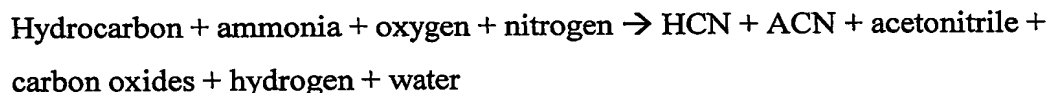
22           FIG. 1e is a schematic view illustrating a system and method, constructed in  
23 accordance with the present invention, with hydrocarbon and ammonia being fed into  
24 separate discharge reactors for generation of the appropriate radicals.

#### 25 26 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

27           Hydrogen cyanide and acrylonitrile are important chemical intermediates used  
28 in a variety of applications of importance in the chemical, pharmaceutical, and mining  
29 industry. The present invention is a system and method for the manufacture of  
30 hydrogen cyanide and acrylonitrile, in particular, as well as acetonitrile. The reactants  
31 – ammonia, and hydrocarbons, for example, methane – are brought into contact in a  
32 single or plurality of pulsed corona or silent barrier discharge reactor(s). The reaction  
33 zone within the discharge reactor may contain suitable catalyst. Air, oxygen and/or

other combinations of nitrogen and oxygen may be added to the feed stream depending on the product stream desired. The walls of the reactor are preferably constructed from membrane materials suitable for the selective continuous removal of hydrogen – formed from the decomposition of the ammonia and hydrocarbon(s) – from the reaction zone. Continuous removal of hydrogen from the reaction zone drives the reaction toward completion, and provides an important product stream.

As described above, the system and method of the present invention is the manufacture of HCN and acrylonitrile, in particular, as well as acetonitrile. The reactants – ammonia, and hydrocarbons, for example, methane – are brought into contact in a single or plurality of pulsed corona or silent barrier discharge reactor(s). The reaction zone within the discharge reactor may contain suitable a catalyst. Air, oxygen and/or other combinations of nitrogen and oxygen may be added to the feed stream depending on the product stream desired. Inert gases, for example, argon and/or helium may be added also to increase the density of ions in the reaction zone. Thus,



Hydrocarbon species used would depend on the final product requirement – examples include methane, ethane, propane, propylene, and ethylene, among others.

Pulsed corona and silent barrier discharge systems do not appear to have been used for these reactions. In these reactors, a non-thermal plasma is formed in the reaction zone, and the reactions of interest are facilitated. Examples of the use of these reactors for other applications – notably in the area of NO<sub>x</sub> destruction, and the treatment of hydrogen sulfide – have been reported. Note that non-equilibrium, or non-thermal, plasmas have been divided into five distinctive groups depending on the mechanism used for their generation, applicable pressure range, and electrode geometry. These are as follows:

- *Glow discharge*: This is an essentially low-pressure phenomenon usually between flat electrodes. The low pressure and mass flow severely restrict chemical industrial application.

- 1     • *Corona Discharge*: Use of inhomogeneous electrode geometries permits  
2       stabilization of discharges at high pressure. Several specific regions of operation –  
3       for example, ac or dc, and pulsed – have been described in the literature for  
4       applications involving, most often, cleanup of flue gas and atmospheric pollutants.  
5       The *AC/DC* corona discharges, however, are inefficient in their higher energy  
6       consumption.
- 7     • *Silent Discharge*: In this operational regime, one or both of the electrodes are  
8       covered with a dielectric layer. Application of a sinusoidal (or other time-varying)  
9       voltage, then, leads to pulsing electric fields and micro-discharges similar to those  
10      observed in pulsed corona discharge systems.
- 11    • *RF Discharge*: In such systems, the electrodes are not an integral part of the  
12      discharge volume. Non-thermal (or non-equilibrium) conditions are expected only  
13      at low pressures, whereas thermal or equilibrium plasmas can be expected at high  
14      pressures – and larger production rates – of interest in the chemical process  
15      industry.
- 16    • *Microwave Discharge*: Here, similar to RF discharge systems, the electrodes are  
17      not an integral part of the discharge volume. The wavelength of the applied  
18      electromagnetic field becomes comparable to the dimensions of the discharge  
19      volume and necessitates other coupling mechanisms.

20

21    In comparing these non-thermal plasmas, it must be noted that in a glow discharge,  
22    the electrons gain energy from the applied field. Due to low pressures, collision with  
23    neutral species is infrequent. Propensity for the creation of reactive ions and chemical  
24    species is limited. Steady state operation is governed, primarily, by loss of energy  
25    incurred by the electrons on enclosure walls and other surfaces within the reactor.  
26    The situation is similar in RF and microwave discharges. In corona and silent  
27    discharges, the situation is *entirely* different – the fast electrons do indeed transfer  
28    energy to other molecules in the system. Electrode geometry and construction prevent  
29    sparking or arcing. The collision between electrons and the molecules leads to the  
30    production of ions and reactive species that facilitates chemical reaction at ostensibly  
31    low temperatures. The pulsing of the corona discharge permits significant reduction  
32    in the power consumption.

1 Another distinguishing feature of the proposed process is the use of pulsed  
2 corona and silent barrier discharge reactors that permit selective removal of hydrogen  
3 from the reaction zone. Many reactions of importance in the process and petroleum  
4 industry are limited by thermodynamic constraints on (closed system) equilibrium  
5 conversion. In such reactions, the reactant conversion can often be enhanced by use  
6 of membrane reactors that operate on the principle of continuous / intermittent  
7 removal of products from the reaction zone. A particularly important category of such  
8 reactors is that based on the use of (catalytic, or non-catalytic) reactors membranes  
9 that are selective to the permeation of hydrogen. This configuration permits  
10 overcoming the equilibrium conversion limitations, and provides a relatively pure  
11 stream of hydrogen that may be

- 12 • recycled to the refinery for use in hydrogenation applications; and / or
- 13 • used as a clean fuel – in a fuel cell, or in direct combustion applications.

14 For example, an inventor of the present application has described the use of pulsed  
15 corona and silent barrier discharge reactors for the decomposition of  $H_2S$ ; the reactor  
16 walls, constructed from hydrogen-permeable membrane materials remove hydrogen  
17 from the reaction zone and serve simultaneously as an electrode. High voltage pulses,  
18 with duration of about tens of nanoseconds, create an intense electric field most in the  
19 reaction zone leading to the formation of a non-thermal plasma. The temperature of  
20 the electrons formed from the ionization of the gaseous medium, as characterized by  
21 electron velocity / energy, is much higher than the temperature of the much larger bulk  
22 gas molecules and other ionic/charged/excited species.

23 Examples of possible configurations are illustrated in FIG. 1. In FIG. 1a, a  
24 hydrocarbon and ammonia are the reactants. FIG. 1b illustrates the inclusion of a  
25 suitable solid phase catalyst within the reaction zone. In FIG. 1c, the addition air,  
26 oxygen, and/or nitrogen is shown; FIG. 1d illustrates a similar feed stream but with  
27 use of a suitable solid phase catalyst in the reaction zone. In FIG. 1e, the hydrocarbon  
28 and ammonia are fed into separate discharge reactors for generation of the appropriate  
29 radicals; these radicals are combined, in the presence of a suitable solid phase catalyst  
30 if necessary, in a separate reaction chamber. Air, oxygen and/or nitrogen may be  
31 added in these reactors. Other combination(s) of such reactors are also possible.

32 The major advantages of the proposed process are as follows:



- 1       • The operation can be carried out at low temperatures with or without the use of  
2       expensive catalyst.
- 3       • The reactor operation can be brought on-line, or shut off, through  
4       instantaneous control of electrical current and voltage, which adds a large  
5       margin of safety to production of this toxic material. Expensive and extensive  
6       clean-up procedures following shutdown, necessary in the conventional  
7       catalytic high-temperature operation, are rendered unnecessary.
- 8       • Removal of hydrogen from the reaction zone permits recovery of a valuable  
9       commodity. It also permits driving the reaction towards completion.
- 10      • The product mix can be controlled readily.

11

12           Reactant conversion or product yield can often be enhanced by use of  
13   membrane reactors that operate on the principle of continuous/intermittent removal of  
14   products from the reaction zone. An important category of such reactors is that based  
15   on the use of membranes that are selective to the permeation of hydrogen. In the  
16   present invention, a system and method is described for the characterization of  
17   hydrogen-permeable membranes. The system and method of the present invention  
18   will, in particular, find application where the permeability of hydrogen has to be  
19   measured for membranes to be used in reactors that employ electrical/electrochemical/  
20   photo-electrochemical fields that lead to generation of hydrogen.

21

22           The foregoing exemplary descriptions and the illustrative preferred  
23   embodiments of the present invention have been explained in the drawings and  
24   described in detail, with varying modifications and alternative embodiments being  
25   taught. While the invention has been so shown, described and illustrated, it should be  
26   understood by those skilled in the art that equivalent changes in form and detail may  
27   be made therein without departing from the true spirit and scope of the invention, and  
28   that the scope of the present invention is to be limited only to the claims except as  
29   precluded by the prior art. Moreover, the invention as disclosed herein, may be  
30   suitably practiced in the absence of the specific elements which are disclosed herein.

31

1

1 CLAIMS

2

3 What is claimed is:

4

5 1. A system for the manufacture of hydrogen cyanide, acrylonitrile, and  
6 acetonitrile, the system comprising:  
7 at least one pulsed corona discharge reactor, each pulsed corona discharge  
8 reactor having a reaction zone; and  
9 at least one product stream containing hydrogen produced in the pulsed corona  
10 discharge reactor and contacting the catalyst;  
11 wherein hydrogen is removed from the reactant to form hydrogen cyanide,  
12 acrylonitrile, and acetonitrile.

13

14 2. The system of claim 1 wherein the pulsed corona discharge reactor has walls,  
15 the walls being constructed from membrane materials suitable for the selective  
16 continuous removal of hydrogen formed from the decomposition of the ammonia and  
17 hydrocarbon(s) in the reaction zone wherein the continuous removal of hydrogen from  
18 the reaction zone drives the reaction to completion.

19

20 3. The system of claim 1 wherein the reactant feed stream has an additive  
21 selected from the group consisting of air, oxygen and other combinations of nitrogen  
22 and oxygen.

23

24 4. The system of claim 1 wherein the reactant feed stream includes ammonia and  
25 hydrocarbons.

26

27 5. The system of claim 4 wherein the hydrocarbons include methane, ethane,  
28 propane, propylene, and ethylene.

29

30 6. The system of claim 1 and further comprising:  
31 inert gases added to the reaction zone for increasing the density of ions in the  
32 reaction zone.

1

2 7. The system of claim 1 wherein the pulsed corona discharge reactor operates on  
3 continuous/intermittent removal of products from the reaction zone.

4

5 8. The system of claim 1 and wherein the reactants are hydrocarbon and  
6 ammonia, a solid phase catalyst is positioned within the reaction zone, and air,  
7 oxygen, and/or nitrogen are added to the feed stream.

8

9 9. The system of claim 1 wherein the reaction zone contains a catalyst.

10

11 10. A system for the manufacture of hydrogen cyanide, acrylonitrile, and  
12 acetonitrile, the system comprising:

13 a pulsed corona discharge reactor; and

14 a feed stream introduced into the pulsed corona discharge reactor;

15 wherein the following reaction is created:

16 hydrocarbon + ammonia + oxygen + nitrogen  $\rightarrow$  HCN + ACN + acetonitrile +  
17 carbon oxides + hydrogen + water.

18

19 11. A method for manufacturing hydrogen cyanide, acrylonitrile, and acetonitrile,  
20 the method comprising:

21 providing at least one pulsed corona discharge reactor, each pulsed corona  
22 discharge reactor having a reaction zone;

23 positioning a catalyst in the reaction zone;

24 introducing at least one reactant feed stream containing hydrogen into the  
25 pulsed corona discharge reactor and contacting the catalyst; and

26 removing hydrogen from the reactant to form hydrogen cyanide, acrylonitrile,  
27 and acetonitrile.

28

29 12. The method of claim 11 and further comprising:

30 constructing the walls of the pulsed corona discharge reactor has walls from  
31 membrane materials suitable for the selective continuous removal of  
32 hydrogen formed from the decomposition of the ammonia and

1 hydrocarbon(s) in the reaction zone wherein the continuous removal of  
2 hydrogen from the reaction zone drives the reaction to completion.

3

4 13. The method of claim 11 and further comprising:  
5 introducing an additive selected from the group consisting of air, oxygen and  
6 other combinations of nitrogen and oxygen into the reactant feed  
7 stream.

8

9 14. The method of claim 11 and further comprising:  
10 adding ammonia and hydrocarbons into the reactant feed streams.

11

12 15. The method of claim 14 wherein the hydrocarbons include methane, ethane,  
13 propane, propylene, and ethylene.

14

15 16. The method of claim 11 and further comprising:  
16 increasing the density of ions in the reaction zone with inert gases added to the  
17 reaction zone.

18

19 17. The method of claim 11 and further comprising:  
20 operating the pulsed corona discharge reactor on continuous/intermittent  
21 removal of products from the reaction zone.

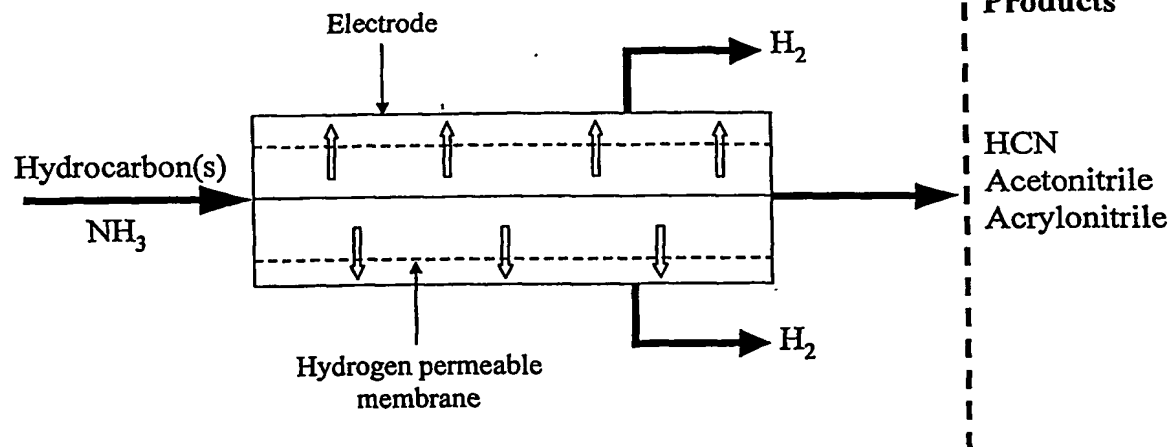
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23 18. The method of claim 11 and wherein the reactants are hydrocarbon and  
24 ammonia, a solid phase catalyst is positioned within the reaction zone, and air,  
25 oxygen, and/or nitrogen are added to the feed stream.

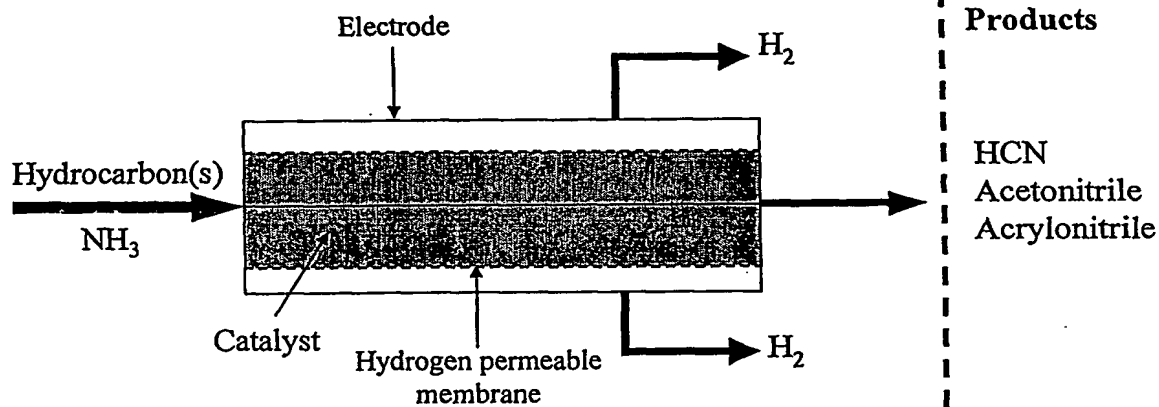
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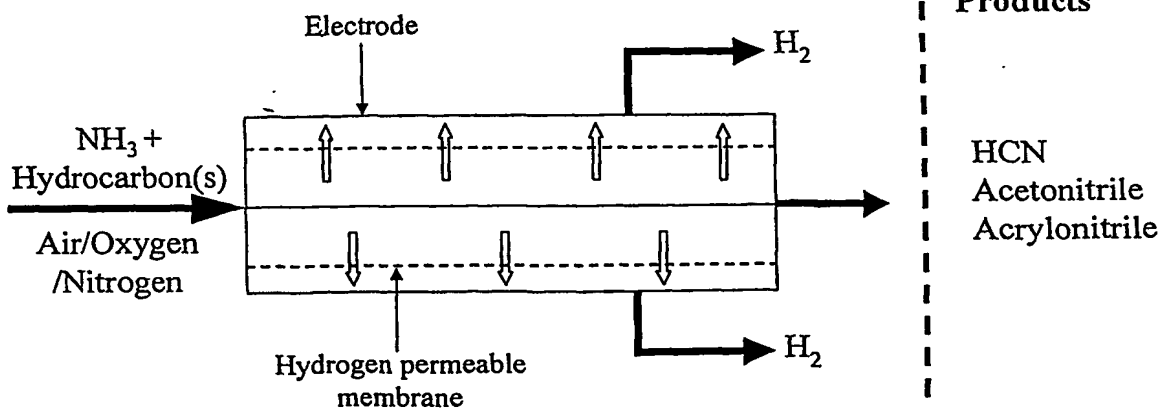
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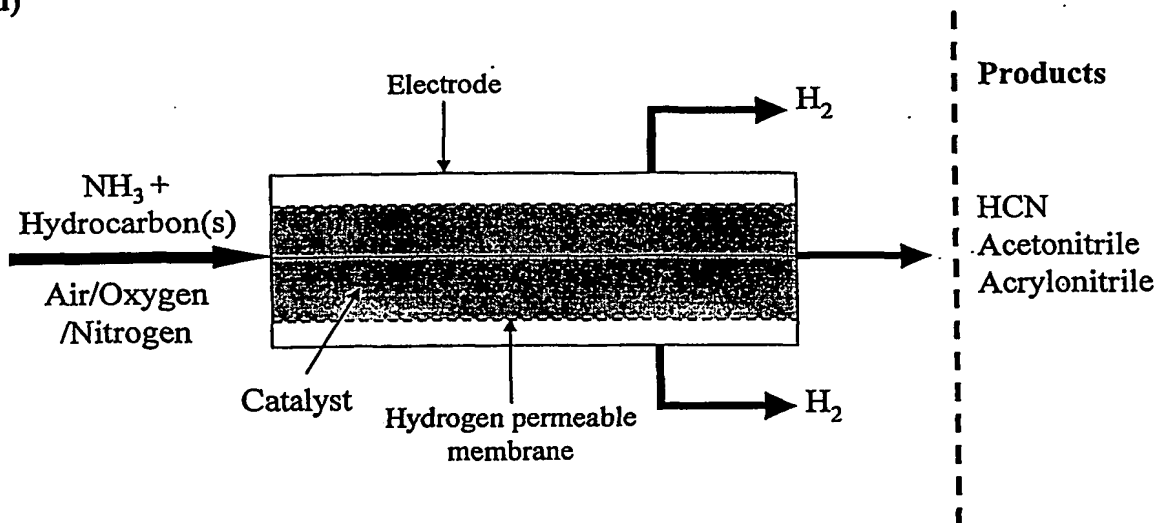
1b)



1c)



1d)



1e)

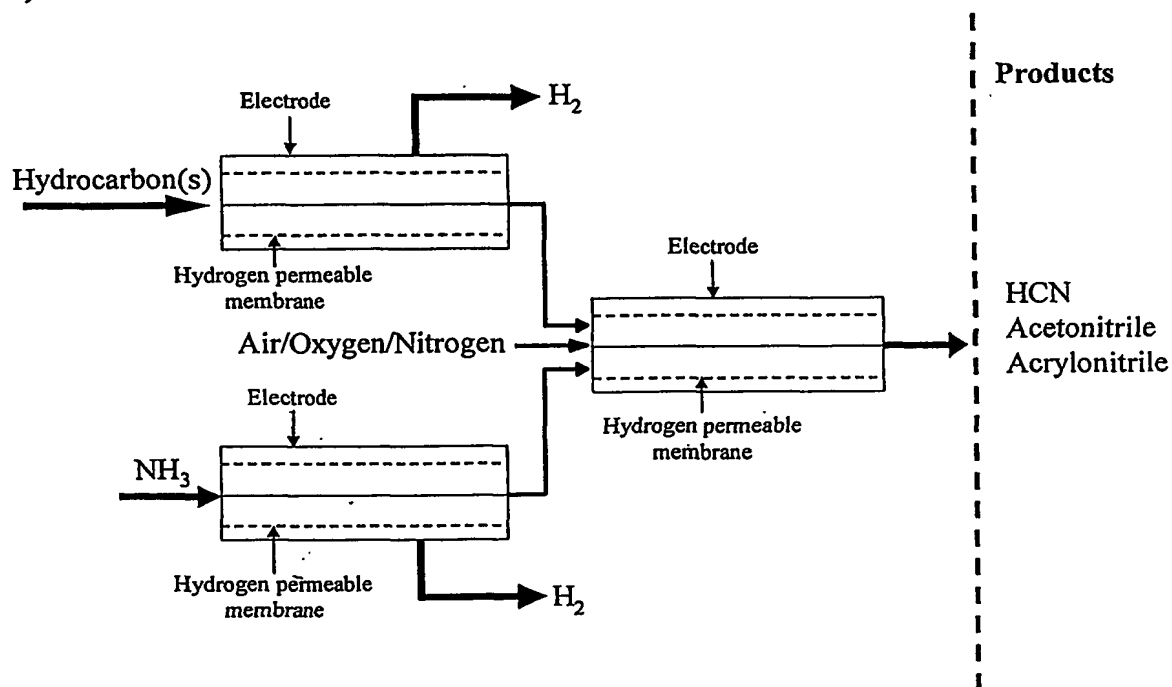


Figure 1: Typical reactor configurations for the synthesis of HCN and ACN

# INTERNATIONAL SEARCH REPORT

International application No.

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<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC(7) : B01J 19/08		
US CL : 422/186.04; 204/164,165		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
U.S. : 422/186.04; 204/164,165		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
WEST; CAPLUS		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,096,173 A (VON HIPPEL et al.) 1 August 2000, see abstract; col. 2, line 66 through col. 3, line 10; col. 3, lines 53-54; col. 1, lines 9-20 and col. 1, line 59 through col. 2, line 2.	1-18
X	US 6,245,309 B1 (ETIEVANT et al.) 12 June 2001, see abstract.	2, 12
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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